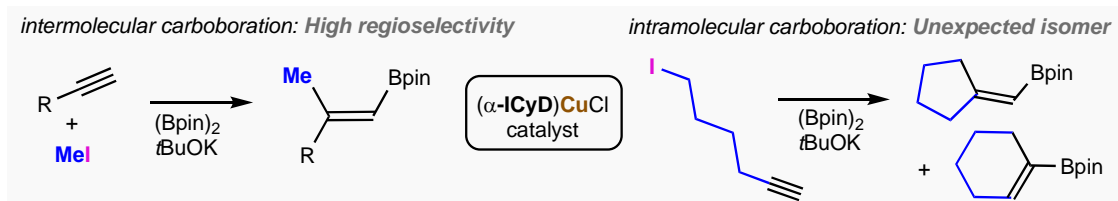
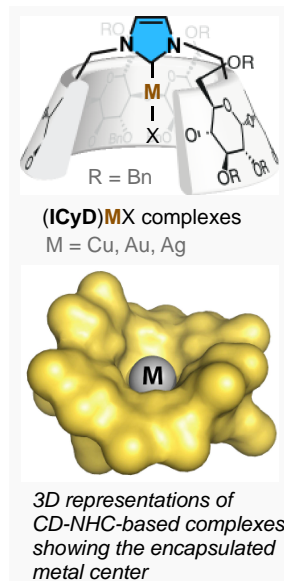


# BORYLATION OF ALKYNES WITH CYCLODEXTRIN-ENCAPSULATED N-HETEROCYCLIC CARBENE COPPER COMPLEXES

S. Roland, Z. Wen, P. Zhang, E. Derat, and M. Sollogoub

Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Paris, France  
sylvain.roland@sorbonne-universite.fr

*Cavity-driven selectivity in organometallic catalysis.* A series of cyclodextrin-based ligands in which the cyclodextrin (CD) is capped with an *N*-heterocyclic carbene (NHC) have been developed for organometallic catalysis.<sup>[1,2]</sup> In CD-NHC-metal complexes, the metal center is deeply encapsulated in the CD cavity. This association of a metal with the hydrophobic CD cavity, which is reminiscent of metalloenzymes, was found particularly favorable for promoting selectivity in catalytic processes. CD-NHC-metal complexes exhibit unique properties due to the variable shapes of the CD cavity induced by NHC capping and to the presence of networks of hydrogen-based weak interactions inside the cavity. Stereoselective gold-catalyzed cyclo-isomerization reactions have been reported with  $\alpha$ - or  $\beta$ -CD-NHC ligands.<sup>[2]</sup> The regioselectivity of some gold-catalyzed cycloisomerization reactions was shown to be dependent on the nature of the cavity ( $\alpha$ - or  $\beta$ -CD-based ligand).<sup>[2]</sup> This particular behavior is not reserved to gold. To further expand the scope of CD-NHC-based ligands (called **ICyDs**), we studied copper-catalyzed reactions. CD-NHC-copper complexes were found to induce interesting control of regioselectivity in alkyne borylation reactions. For instance, the regioselectivity of the hydroboration reaction was shown to be opposite from an  $\alpha$ -CD-derived to a  $\beta$ -CD-derived complex.<sup>[3]</sup> In addition, we found that the cavity could enhance the regioselectivity of intermolecular alkylboration reactions. For intramolecular carboboration reactions, an unprecedented regioselectivity was observed. We accidentally found that CD-NHC or "classical" NHC ligands induced the formation of unexpected six-membered vinylborane derivatives.<sup>[4]</sup> The details of copper-catalyzed borylation reactions with **ICyD** ligands will be presented.



Examples of copper-catalyzed reactions with CD-NHC ligands (**ICyD**).

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[4] Z.-H. Wen, Y. Zhang, S. Roland, M. Sollogoub, *Eur. J. Org. Chem.* 2019, <https://doi.org/10.1002/ejoc.201900246>.